Review and Validation of Hourly VOC Data Collected by PAMS AutoGC Systems

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National Ambient Air Quality Standards (NAAQS) Rule

"Following the directives of the Clean Air Act (CAA), on October 1, 2015, Administrator McCarthy signed a rulemaking action that revises the current national ambient air quality standards (NAAQS) for ozone to a new, more protective level of 0.070 parts per million (70 parts per billion)."

-From EPA Memorandum re: Implementing the 2015 Ozone National Ambient Air Quality Standards, 1 Oct 2015

Changes to PAMS VOC monitoring requirements:

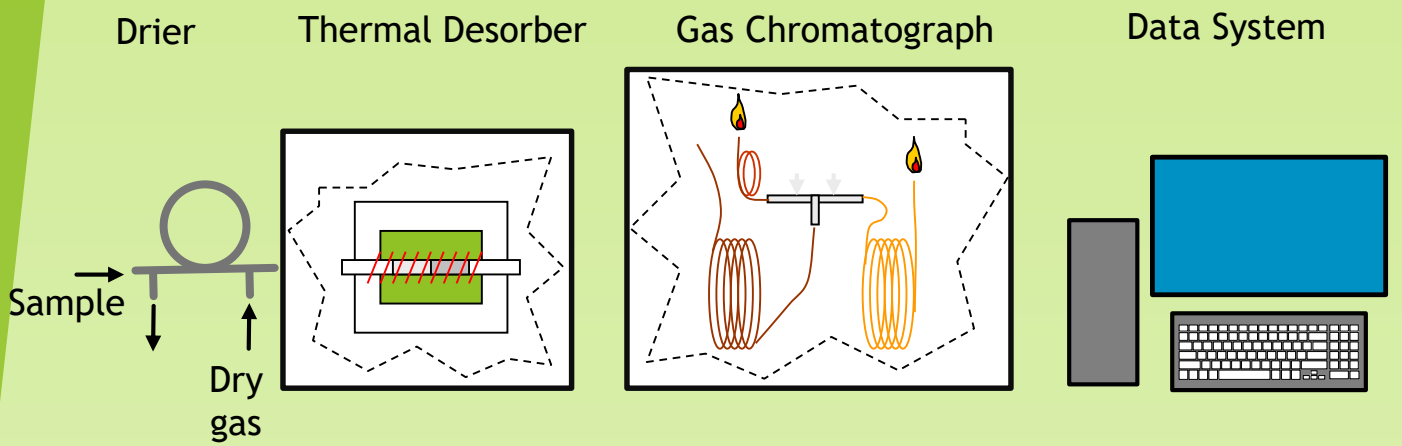
- Redistribution of sites – NCore sites in CBSA > 1 million
  - Additional monitors based on State EMPs for non-attainment areas
- Continuous Monitoring – canister samples only on waivers
- Hourly sampling only for ozone season

AutoGC Systems
Continuous Monitoring June-August

- Key objectives of revised PAMS monitoring
  - Data to support the development of air quality models
  - Data to track continuing trends in air quality
- Data Collected will be archival in nature
  - Validation and review is a key element to the collection of data for use in future evaluations across sites and years.
  - Use of frequent quality checks to eliminate data losses.
  - Strong and unified quality assurance plan to insure data is uniform across sites.

AutoGC Systems: Data Management
Hourly Sample Collection and Separation

Laboratory Quality Analysis in the Field:
PerkinElmer and Agilent solutions configured by Orsat



Sample Collection
Thermal Desorber

→

Data Acquisition
Gas Chromatograph

→

Data Processing
Chromatography
Data System

↓

Data Files and
ASCII text files

→

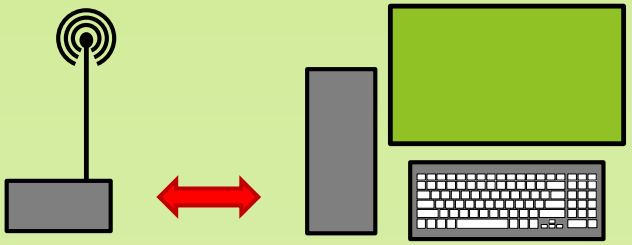
Mmove.exe
Archives original data
Copies text file and
data for polling

↑

Broadband Connection
Polling and Remote
operations

AutoGC Systems: Data Management
Hourly Sample Collection and Separation

Data Validation Site: Review, validate and generate AQS Files



Broadband Connection
Polling Remote sites to retrieve data

Validation Data System for review of data

Cloud Service or Database for Review of Quality Control Checks and Ambient Data

Data Loaded into Database for Review

Data Review QuickLooks
QC and control charts
Ambient Data

Chromatography Review
Review chromatograhic data

Data Reprocessing, if necessary, Reloaded and Reviewed

Data Flagged and AIRS file generation

AutoGC Systems: Data Management
Data Collection June to August

- Data Quality Objectives
  - Bias 25%
  - Precision 15-25%
  - Detection Limit 0.5 ppbC
  - Completeness 80% *
- Routine QC Data Collected
  - Total hourly samples = 2208 (92 days)
  - Daily Check Samples = 105
  - Blanks = 92
  - Retention time checks = 13
  - Laboratory Check Samples = 13
  - Ambient data = 1985/2208

• after adjustment for routine required quality control samples (10.1%).

AutoGC Systems

- Key Issues Associated with Continuous Field Analysis
  - Hourly sample period consistent with other criteria measurements, NOx, O^3
    - Power failures
    - Ambient temperatures
  - Accurate and repeatable target identification, retention time stability
    - Moisture related issues
    - Concentration related issues
  - Repeatable quantitation, changes in sensitivity, drift
    - System failures related to sampling times
    - Power failures
    - Sample pump failures

AutoGC Systems
Automated Quality Control Checks

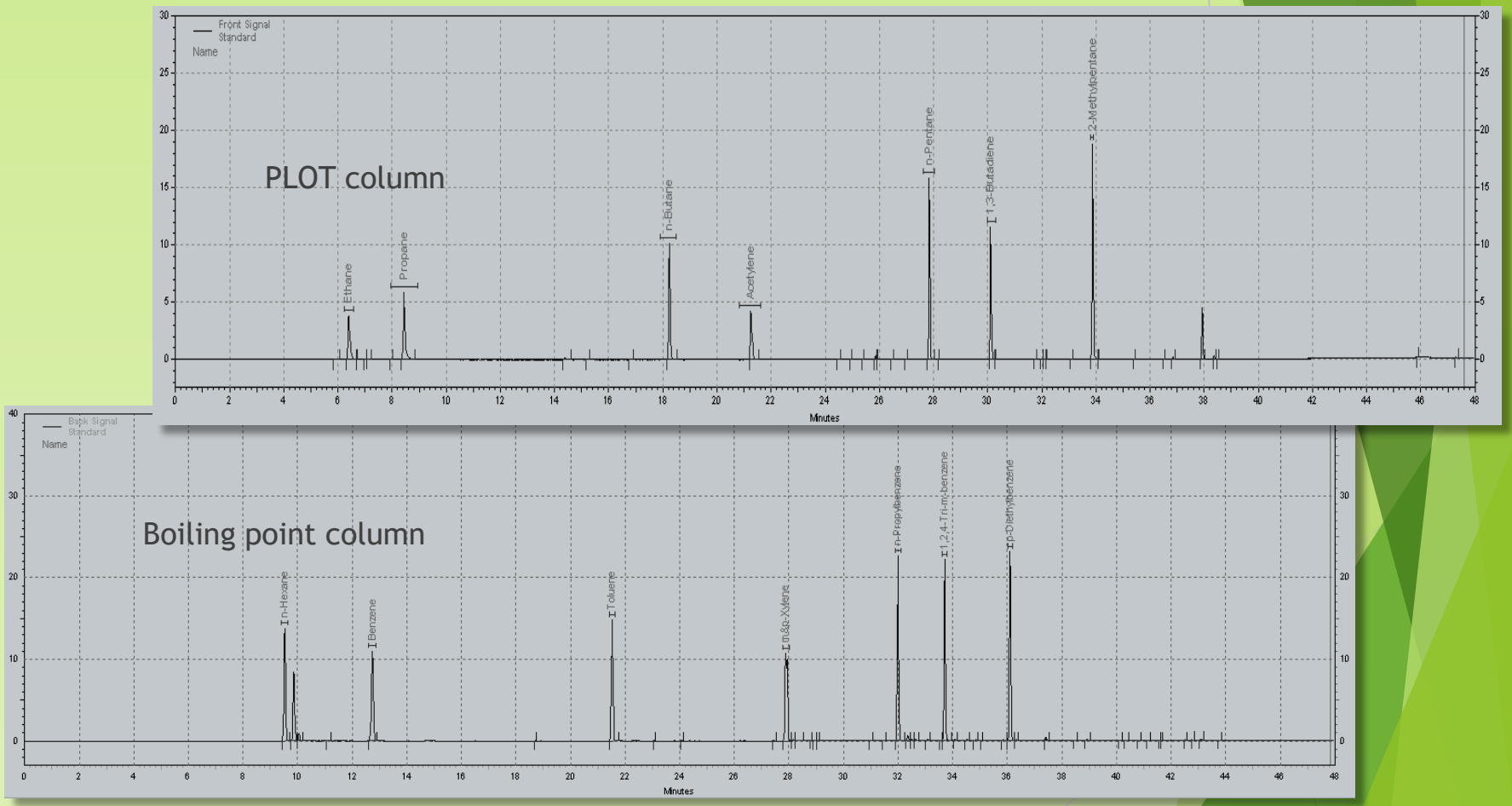
Quality Control Check	Composition	Purpose	Frequency	Acceptance Criteria
Retention Time Standard (RTS)	Mixture containing all target compounds ideally between 1-5 ppbC	To help assess retention time shifts and optimize processing methods	Twice a month or weekly	100% of the compounds are identified correctly in the multicomponent RTS
Calibration Verification Sample (CVS)	Mixture of 15 reference compounds including Propane and Benzene used for calibration	To assess the instrument drift and ensure continued instrument calibration	Daily	1) Propane and Benzene % recoveries within 75% - 125% and all other calibrants within 55 - 145%
				2) Data must be bracketed by valid CVS
Method (Analytical) Blank	Humidified, clean air	To assess system contribution to the measurement	Daily	1) All target compounds < 2.0 ppbC
				2) TNMHC < 20 ppbC
				3) Data must be bracketed by valid blanks
Precision Check	Mixture used for CVS	To assess analytical precision	Weekly	Propane and Benzene %RPD < 20% in two consecutive CVS runs
Laboratory Calibration Sample (LCS)	Mixture of 15 reference compounds including Propane and Benzene used for calibration	Second source standard, statically blended 5 ppbv	Twice a month or weekly	Propane and Benzene % recoveries within 70-130%

AutoGE Systems:
Additional Automation for Introduction of Quality Control Samples

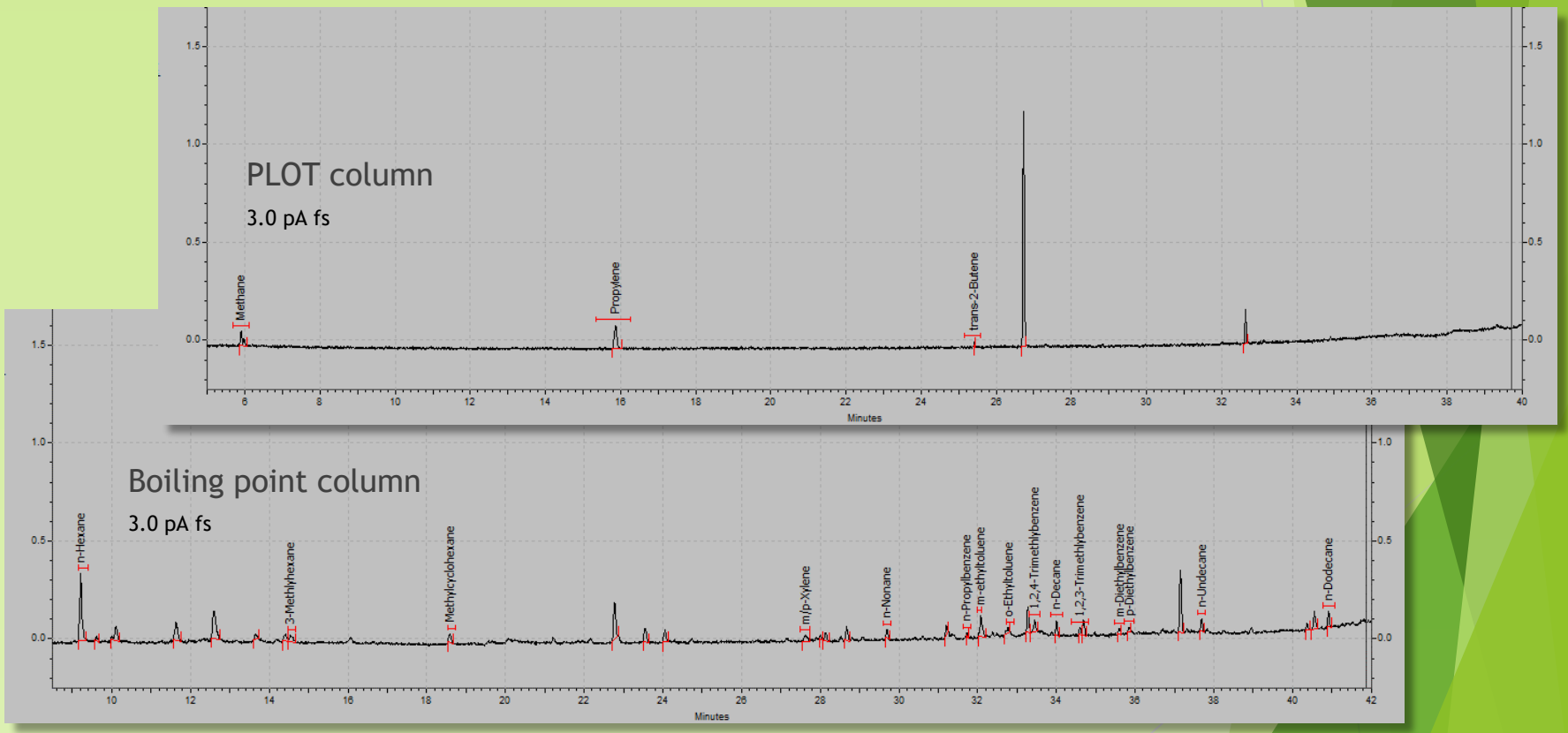
- Automatic introduction of QC samples
  - Dynamically diluted check sample
  - Analytical blank
- Manual dilution of multipoint calibration curve
- Dilution from 100 ppbv or 1 ppmv multi-component standard

Daily Check Sample

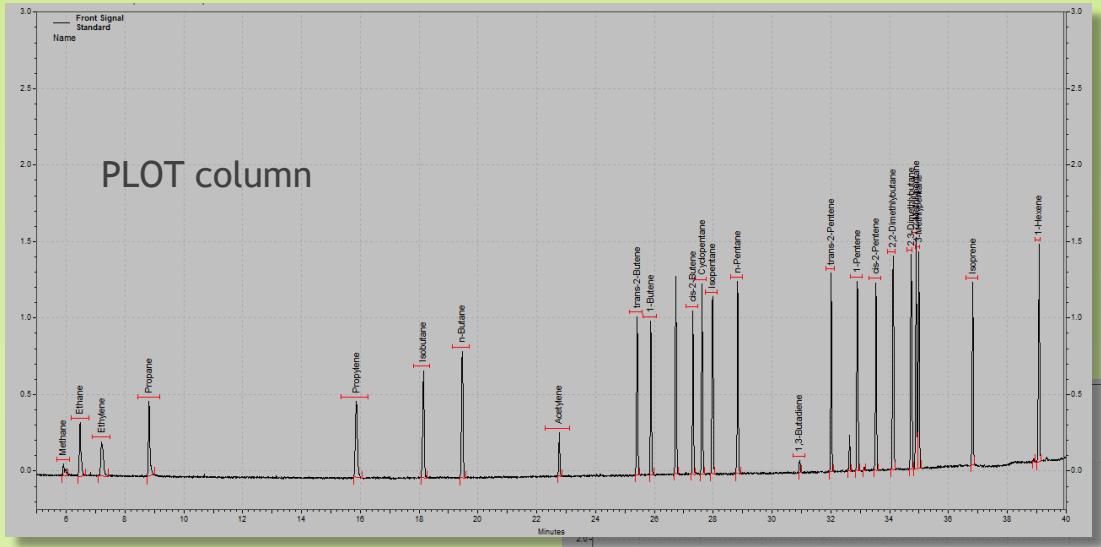
Dynamic dilution from 1 ppmv to 5 ppbv



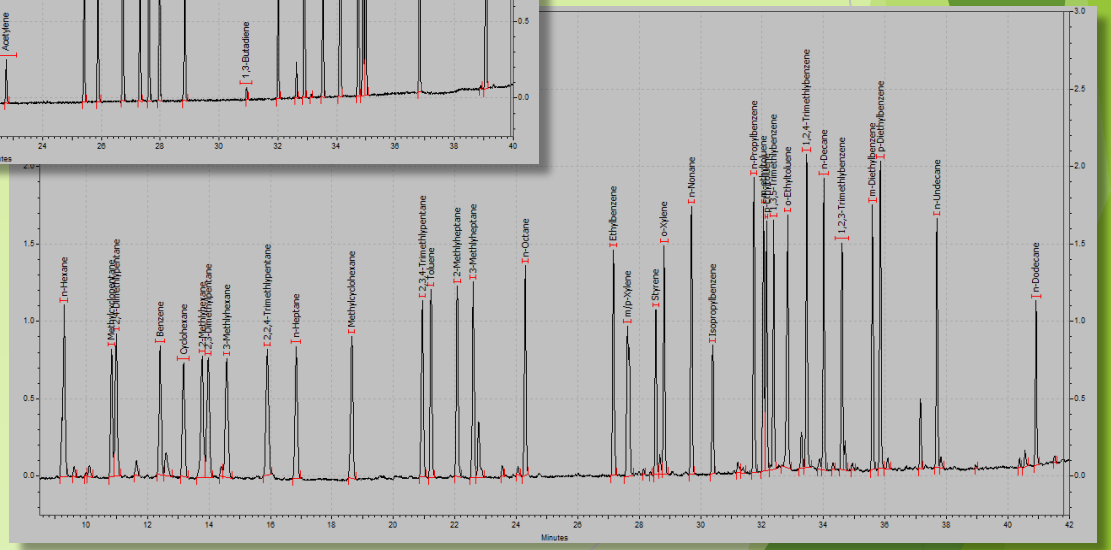
Analytical Blank
Dilution system zero diluent



Retention Time Standard
“spike” in zero air



Boiling point column

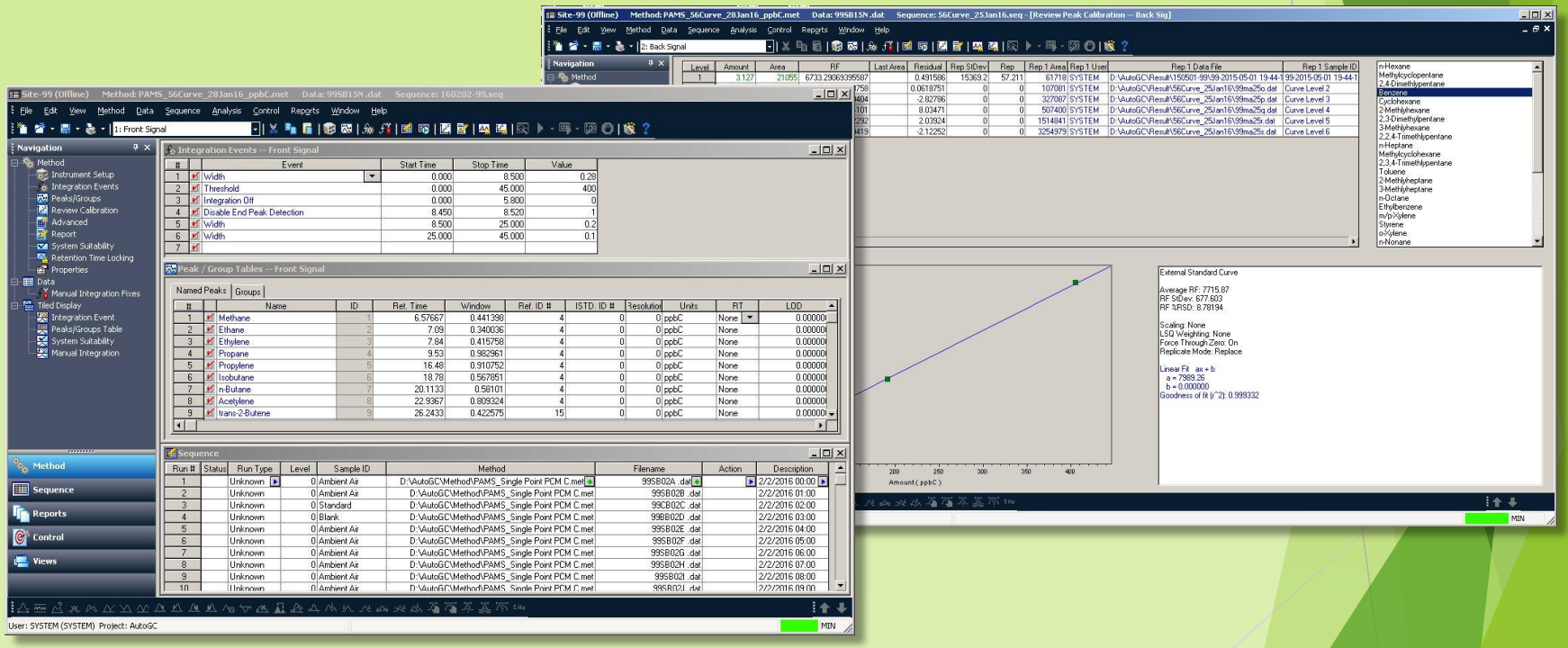


AutoGC Systems
Chromatography Data Systems

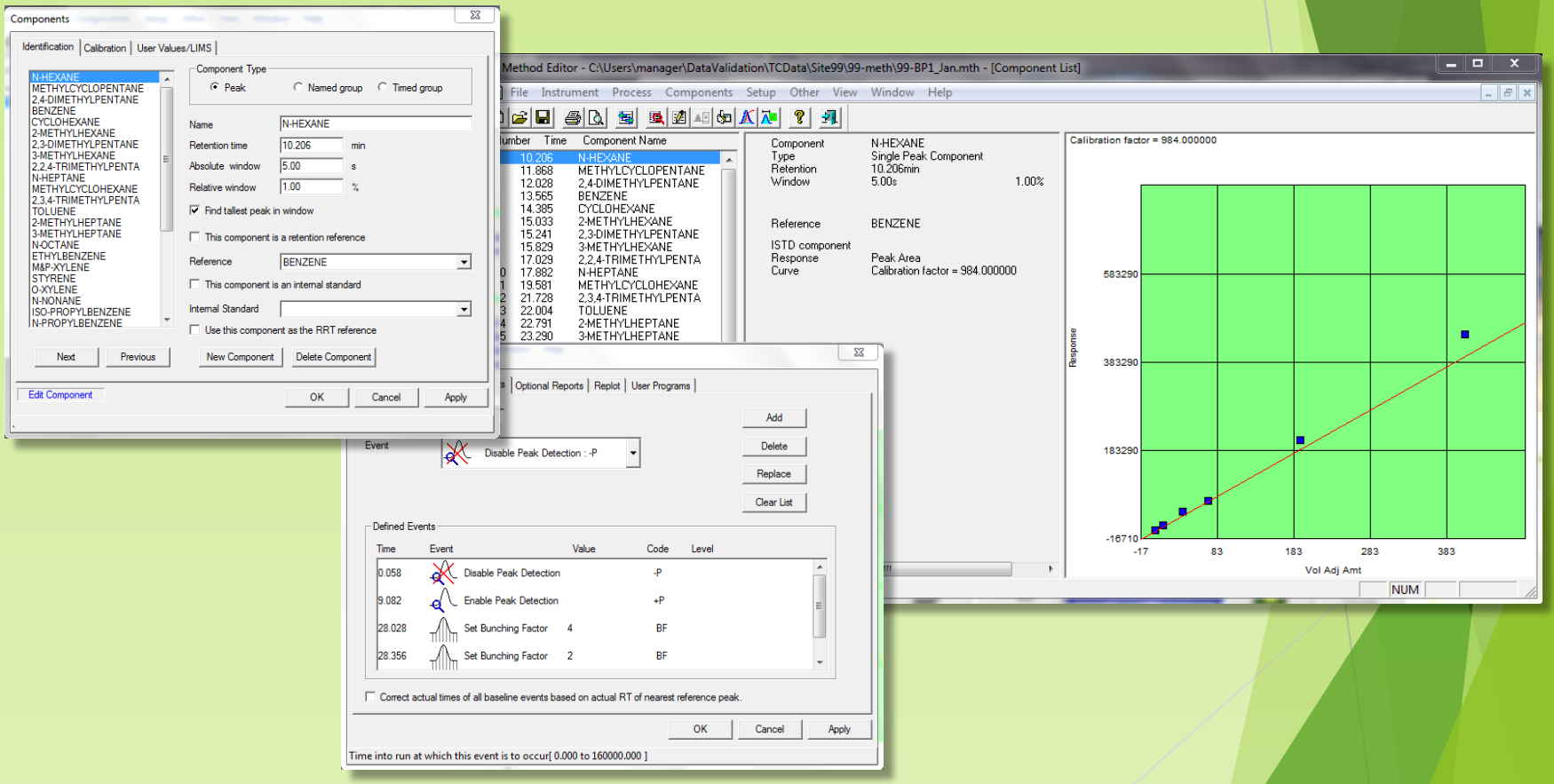
Requirements:

- Data portability
- Ability to reconstruct the original processing method from result
- Use of Retention time references to accommodate diurnal shifts
- Use of response factors and calibration by reference for unidentified HCs
- Ability to name files for easy identification of site, date, time, hour and sample type
- Ability to schedule and control introduction of routine quality control samples
- Ability to recover from simple power failures and continue hourly sampling

Method Development
EZChrom Chromatography Data System



Method Development
TotalChrom Chromatography Data System



AutoGE Systems
Meeting Data Quality Objectives

Operations

- Well defined Operating Procedures
- Well documented instrumental parameters
- Fully automated system to reduce errors in operator activities
- Easily identifiable and transportable data files
- Fully automated Quality Checks

Data Validation

- Well defined Quality Control Limits
- Real-time data transfer and review
- Well defined validation operating procedures
- Good annual audits to review instrument performance across network.

AutoGE Systems
Data Review – Data Validation

Data Review - Daily

- Site Operations
  - On-time collection
  - Correct identification
  - Equipment parameters
- Quality Controls
  - Passing Blanks
  - Passing check sample recovery

Data Validation - Monthly

- Review of Quality Controls
  - Passing check sample recoveries – flagging
  - Passing blanks – flagging failed targets
  - Retention time checks
- Review of Ambient Data
  - Review of high hours or other issues
  - Review data for internal consistency

AutoGC Systems
Validation Levels
PAMS Data Analysis Workbook: Data Validation

Level 0 – Routine Data Checks

- Sampling errors
- Instrumental failures

Level 1 – Evaluation of Quality Control Data

- Pass/Fail criteria for daily checks
- Review of target identification
  - Use time series plots to evaluate outliers
  - Use retention time plots to determine misidentifications

Level II – Temporal and Spacial Consistency

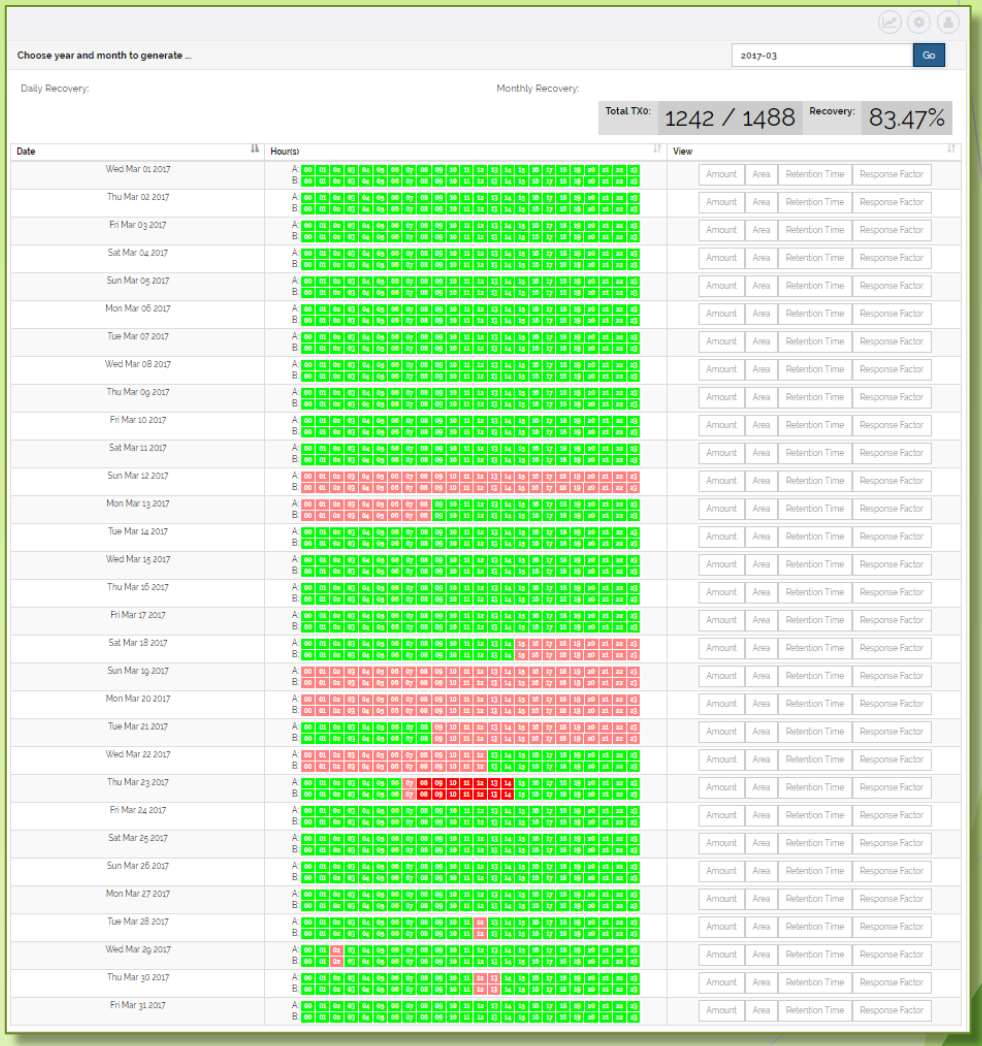
- Abundant species present
- Diurnal patterns
- Statistical evaluation of historical data

Level III – External Verifications

- Second source static dilution
- Co-located collection results
- Performance Audits

AutoGC Systems: Level 0 Data Review

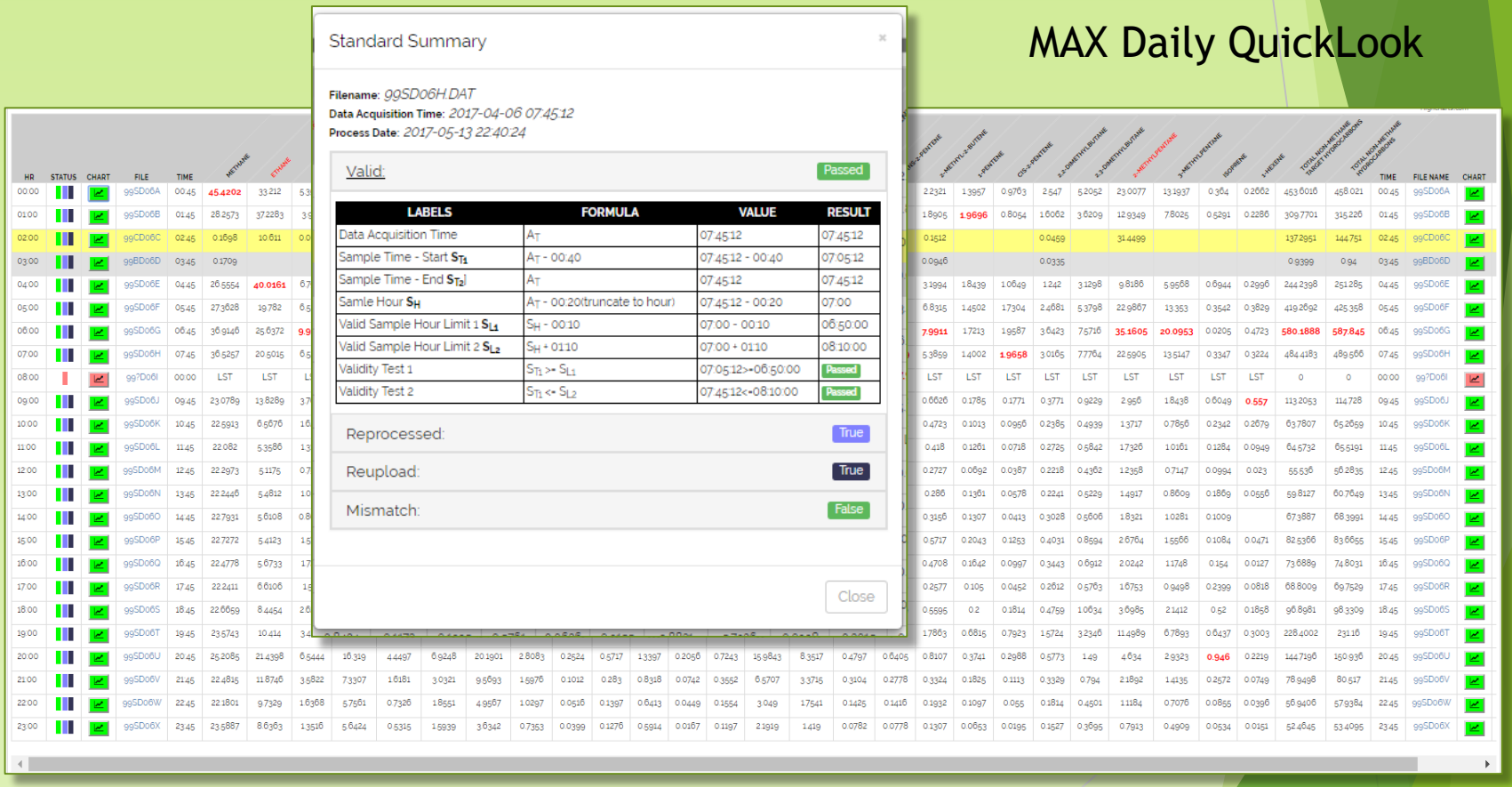
Verify sampling
Lost Data



AutoGC Systems: Level 0 Data Review

Verify sampling – incorrect sampling interval

MAX Daily QuickLook



Standard Summary

Filename: *99SD06H.DAT*
Data Acquisition Time: *2017-04-06 07:45:12*
Process Date: *2017-05-13 22:40:24*

Valid: Passed

LABELS	FORMULA	VALUE	RESULT
Data Acquisition Time	A_T	07:45:12	07:45:12
Sample Time - Start S_{T1}	A_T - 00:40	07:45:12 - 00:40	07:05:12
Sample Time - End S_{T2}	A_T	07:45:12	07:45:12
Samle Hour S_H	A_T - 00:20(truncate to hour)	07:45:12 - 00:20	07:00
Valid Sample Hour Limit 1 S_{L1}	S_H - 00:10	07:00 - 00:10	06:50:00
Valid Sample Hour Limit 2 S_{L2}	S_H + 01:10	07:00 + 01:10	08:10:00
Validity Test 1	S_{T1} >= S_{L1}	07:05:12>=06:50:00	Passed
Validity Test 2	S_{T1} <= S_{L2}	07:45:12<=08:10:00	Passed

Reprocessed: True

Reupload: True

Mismatch: False

Close

AutoGC Systems: Level I Data Review

QuickLook Daily Check Sample

Channel A: CVS Concentration (2017-05-20)

Cylinder: CC344433 **Date On:** 2017-02-21 00:00:00 **Date Off:** 2017-06-02 15:59:59 **Dilution Factor:** 0.00483
[Propane RF = 13195**]**

NAME	CARBON NUMBER	CERT CONC (PPMV)	CALC DILUTED CONC (PPBC)	MEASURED CONC 1 (PPBC)	RUN 1 % RECOVERY (99CE20C.DAT)	RECOVERY MIN/MAX
ETHANE	2	1.09	10.53	11.34	107.66	55/145
PROPANE	3	1.04	15.07	15.70	104.21	75/125
N-BUTANE	4	1.09	21.06	21.99	104.44	55/145
ACETYLENE	2	1.09	10.53	7.05	66.92	55/145
N-PENTANE	5	1.07	25.84	26.90	104.11	55/145
1,3-BUTADIENE	4	1.06	20.48	21.05	102.78	55/145
2-METHYLPENTANE	6	1.04	30.14	32.24	106.96	55/145

Blank Run: (99BE20D.DAT) 0.4572

Channel B: CVS Concentration (2017-05-20)

Cylinder: CC344433 **Date On:** 2017-02-21 00:00:00 **Date Off:** 2017-06-02 15:59:59 **Dilution Factor:** 0.00483
[Benzene RF = 12828**]**

NAME	CARBON NUMBER	CERT CONC (PPMV)	CALC DILUTED CONC (PPBC)	MEASURED CONC 1 (PPBC)	RUN 1 % RECOVERY (99CE20C.DAT)	RECOVERY MIN/MAX
N-HEXANE	6	1.08	31.30	33.02	105.5	55/145
BENZENE	6	1.10	31.88	32.54	102.07	75/125
TOLUENE	7	1.10	37.19	37.61	101.11	55/145
M&P-XYLENE	8	1.10	42.50	42.44	99.85	55/145
N-PROPYLBENZENE	9	1.03	44.77	46.62	104.12	55/145
1,2,4-TRI-M-BENZENE	9	1.07	46.51	45.70	98.26	55/145
P-DIETHYLBENZENE	10	1.00	48.30	47.11	97.54	55/145

Blank Run: (99BE20D.DAT) 9.1965

QuickLook Weekly Static 2nd Source Check Sample

Channel A: LCS Concentration (2017-05-20)

Cylinder: AAL7395 **Date On:** 2016-01-01 00:00:00 **Date Off:** In Use **Dilution Factor:** 0.00548
[Propane RF = 13195**]**

NAME	CARBON NUMBER	CERT CONC (PPMV)	CALC DILUTED CONC (PPBC)	MEASURED CONC 1 (PPBC)	RUN 1 % RECOVERY (99EE20V.DAT)	RECOVERY MIN/MAX
ETHANE	2	1.06	11.62	9.20	79.22	70/130
PROPANE	3	0.99	16.28	13.63	83.77	70/130
N-BUTANE	4	0.98	21.48	17.46	81.3	70/130
ACETYLENE	2	0.99	10.85	9.19	84.67	70/130
N-PENTANE	5	1.04	28.50	22.61	79.34	70/130
1,3-BUTADIENE	4	0.92	20.17	17.15	85.03	70/130
2-METHYLPENTANE	6	0.96	31.56	27.84	88.2	70/130

Blank Run: (99BE20D.DAT) 0.4572

Channel B: LCS Concentration (2017-05-20)

Cylinder: AAL7395 **Date On:** 2016-01-01 00:00:00 **Date Off:** In Use **Dilution Factor:** 0.00548
[Benzene RF = 12828**]**

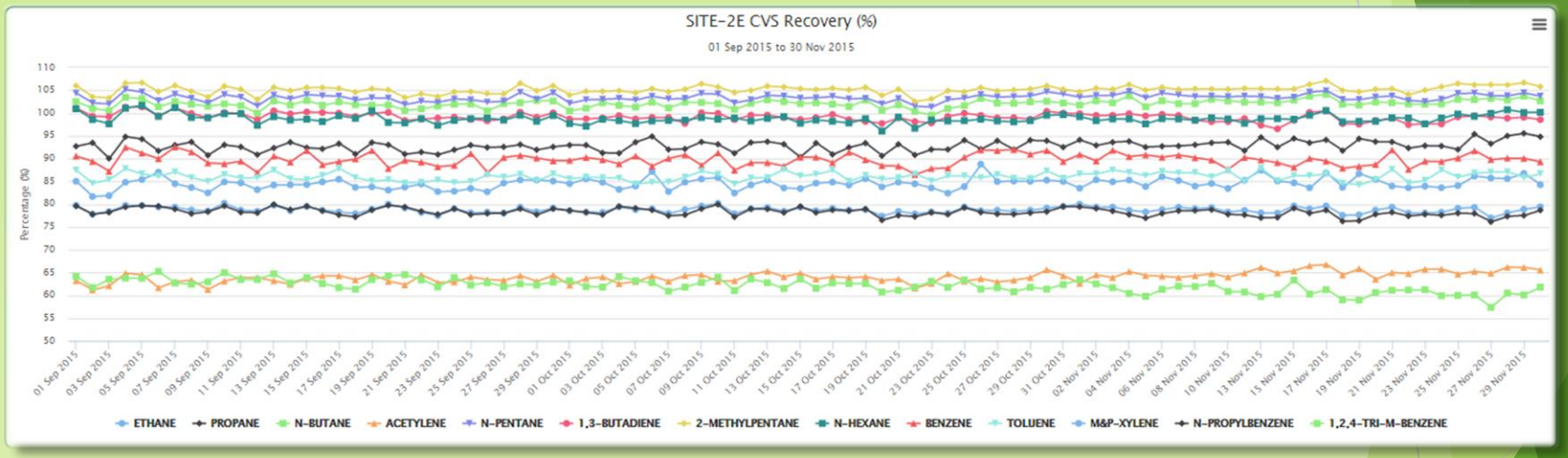
NAME	CARBON NUMBER	CERT CONC (PPMV)	CALC DILUTED CONC (PPBC)	MEASURED CONC 1 (PPBC)	RUN 1 % RECOVERY (99EE20V.DAT)	RECOVERY MIN/MAX
N-HEXANE	6	1.00	32.88	27.92	84.93	70/130
BENZENE	6	1.05	34.52	27.69	80.22	70/130
TOLUENE	7	1.05	40.28	32.44	80.54	70/130
M&P-XYLENE	8	0.97	42.52	37.53	88.26	70/130
N-PROPYLBENZENE	9	1.02	50.31	42.49	84.46	70/130
1,2,4-TRI-M-BENZENE	9	0.95	46.85	41.23	87.99	70/130
P-DIETHYLBENZENE	10	0.95	52.06	44.74	85.94	70/130

Blank Run: (99BE20D.DAT) 9.1965

AutoGC Systems: Level I Data Review

Calibration Verification Sample (CVS)

Dynamically Diluted Daily Check Sample

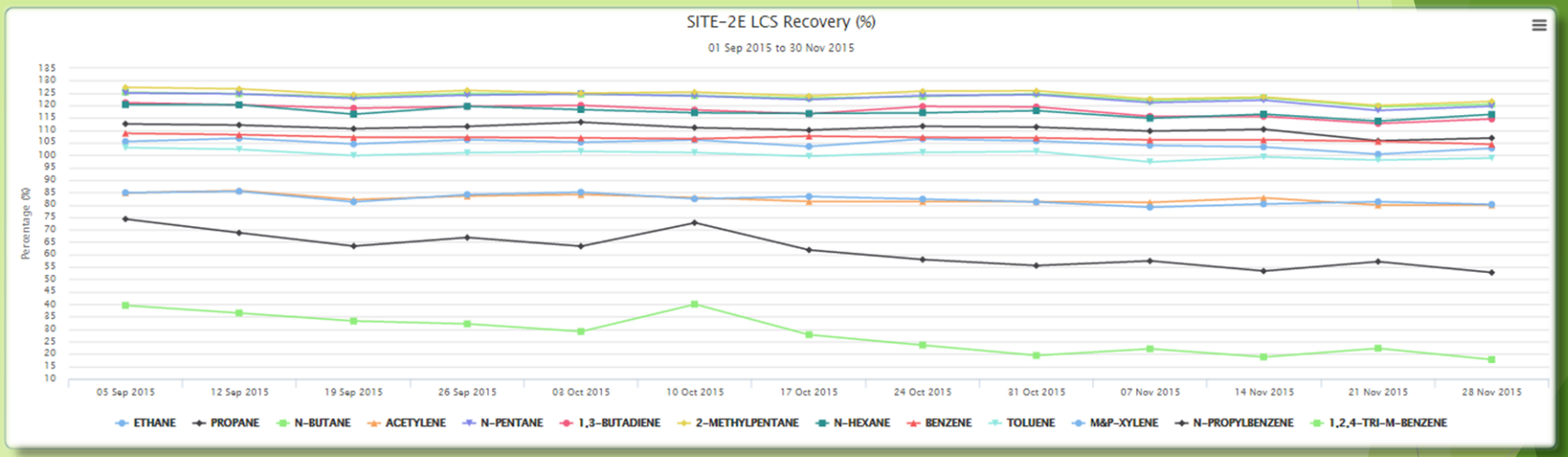


Recoveries based on carbon response for Propane or Benzene

AutoGC Systems: Level I Data Review

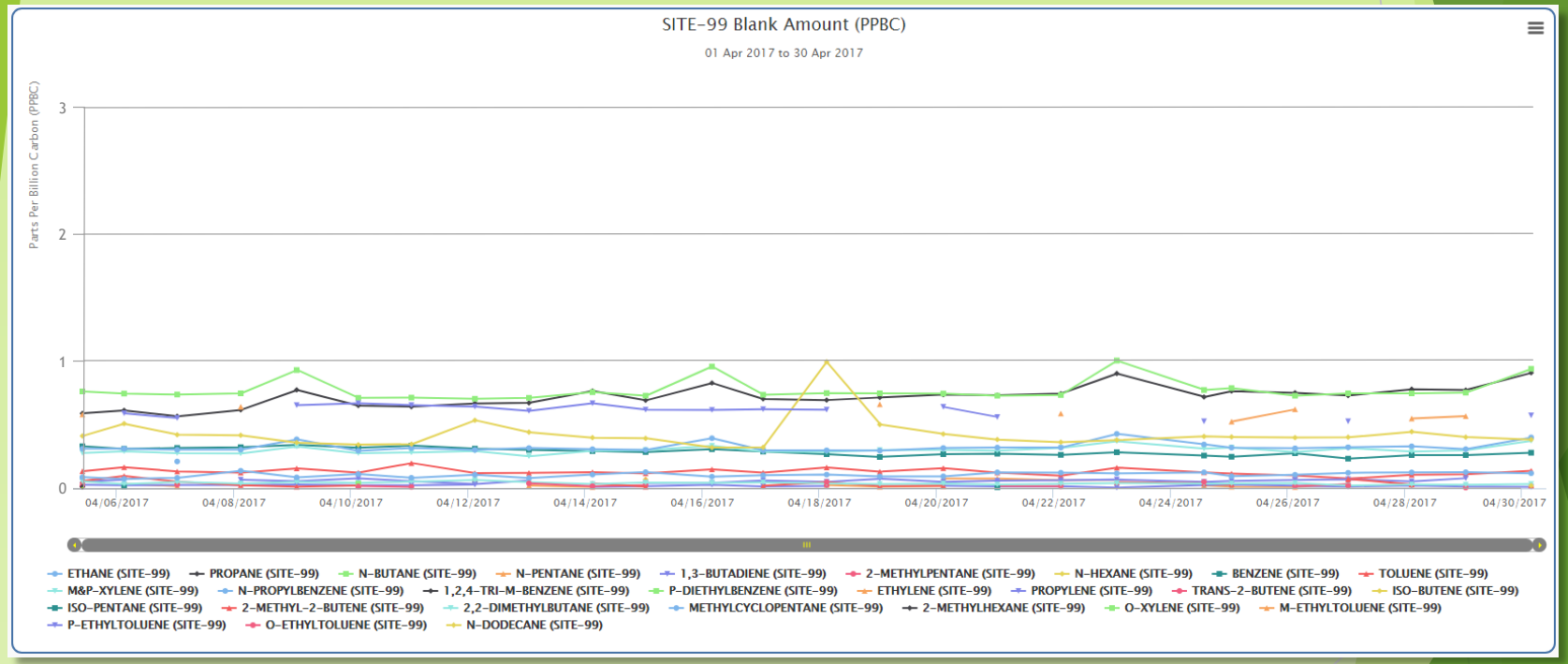
Laboratory Control Sample (LCS)

Weekly Static Dilution Canister Sample



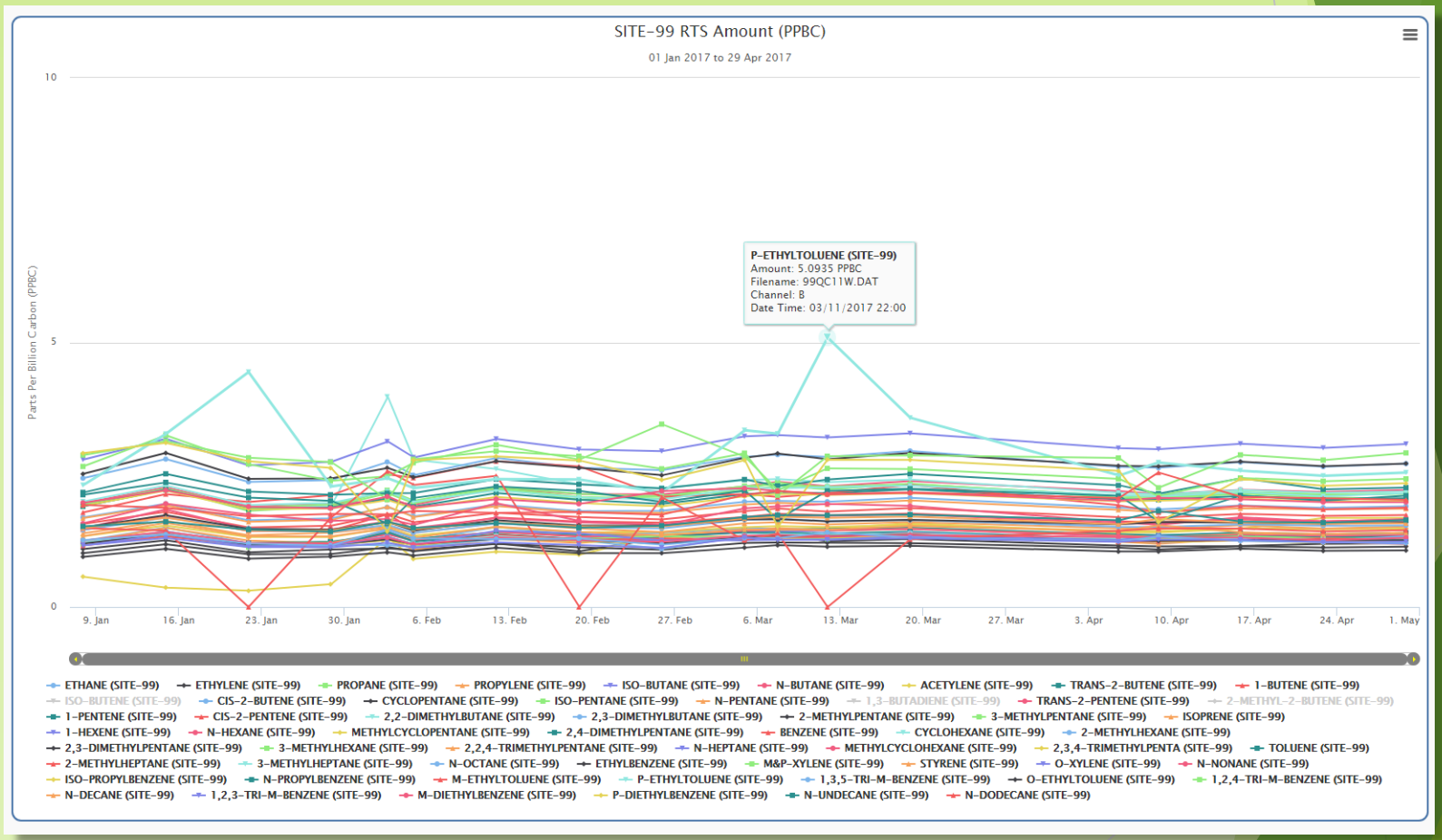
AutoGC Systems: Level I Data Review

Daily Blank Sample



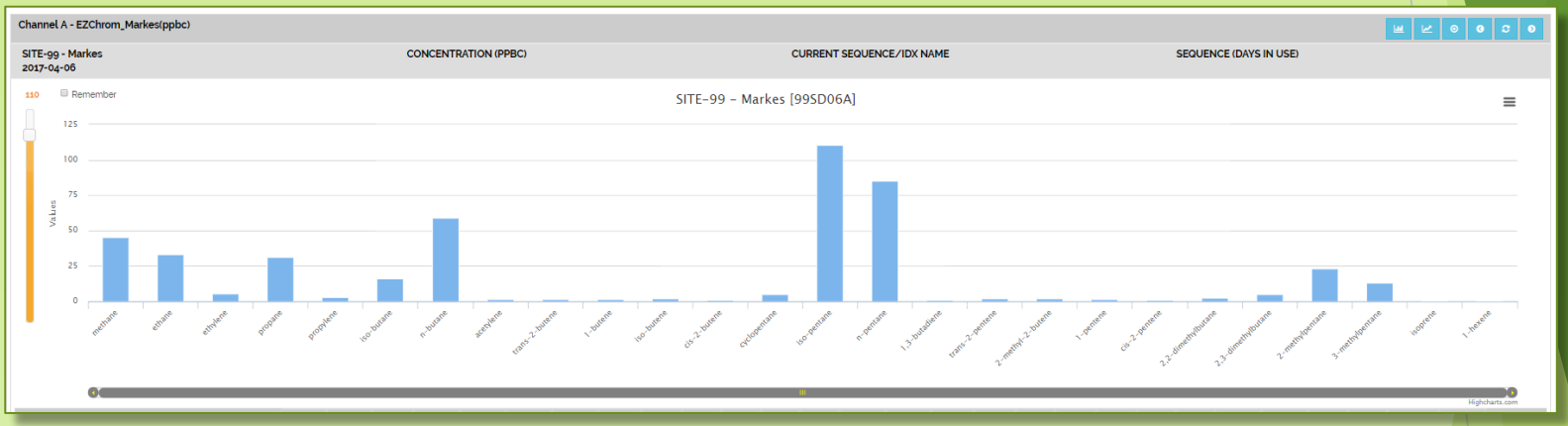
AutoGC Systems: Level I Data Review

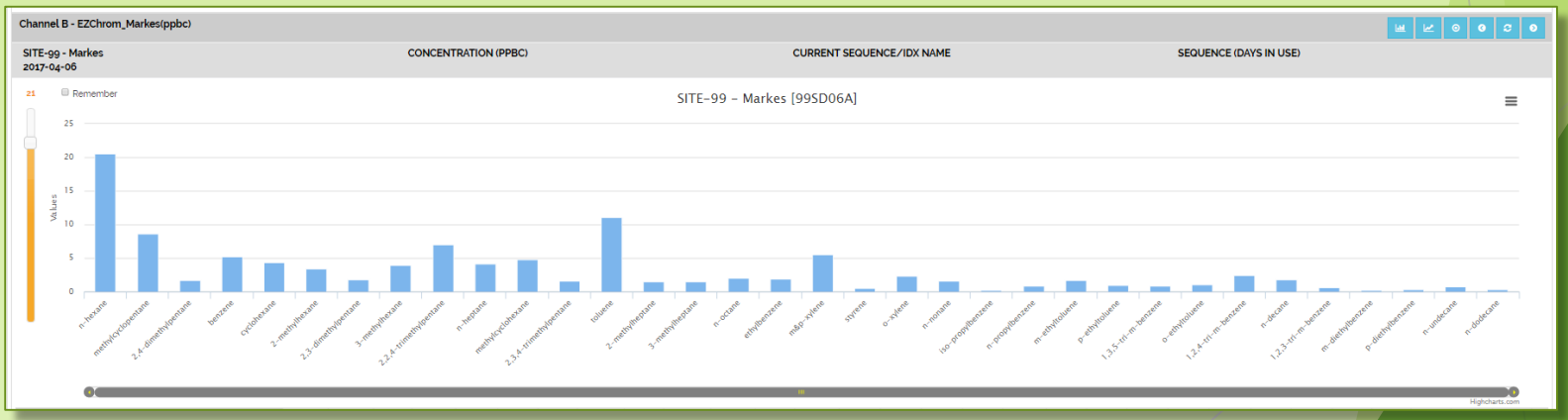
Retention Time Standard – Target Identification



AutoGC Systems: Level II Data Review

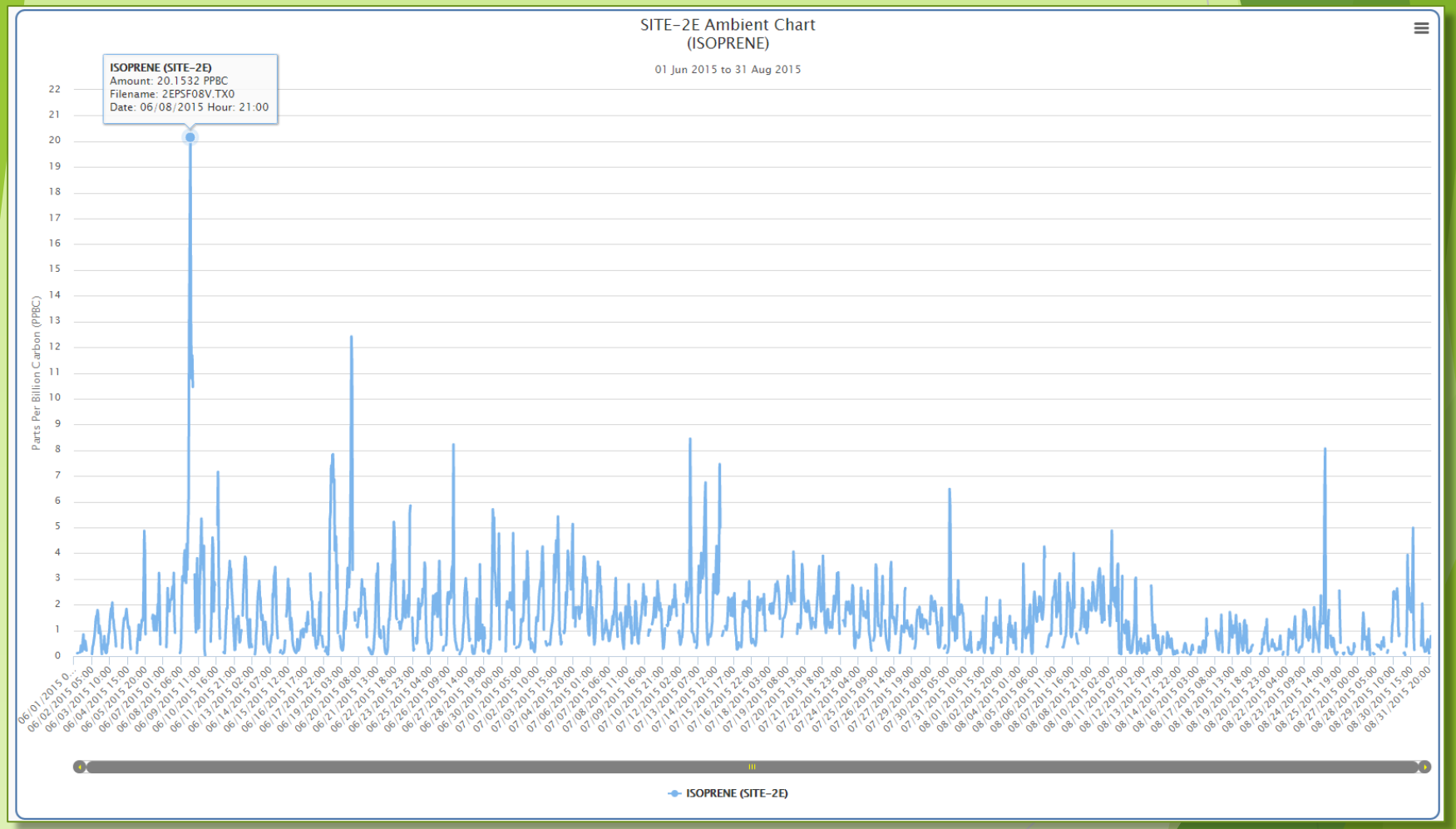
Abundant Species





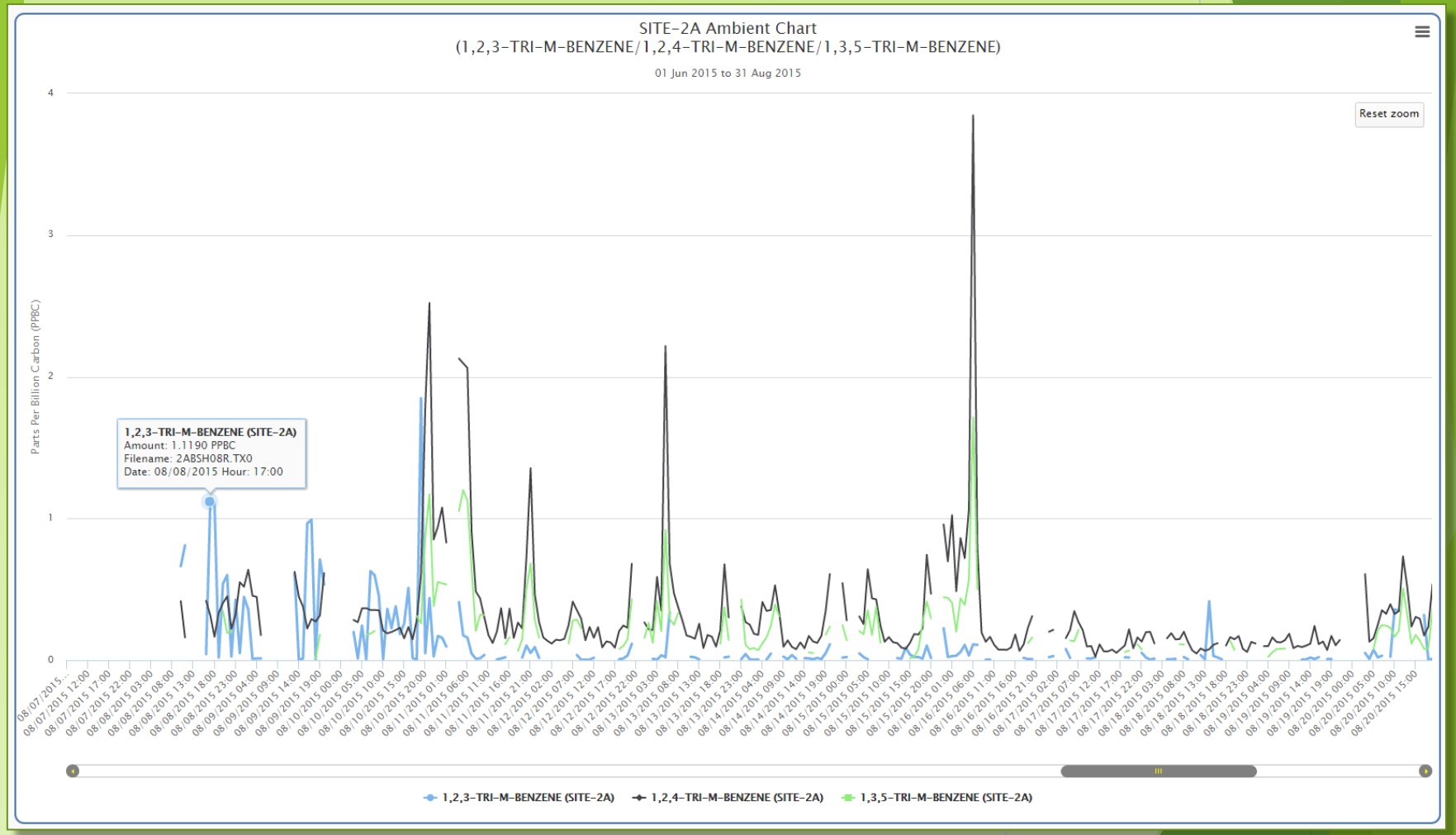
AutoGC Systems: Level II Data Review

Ambient Data – Time Series – Diurnal Patterns



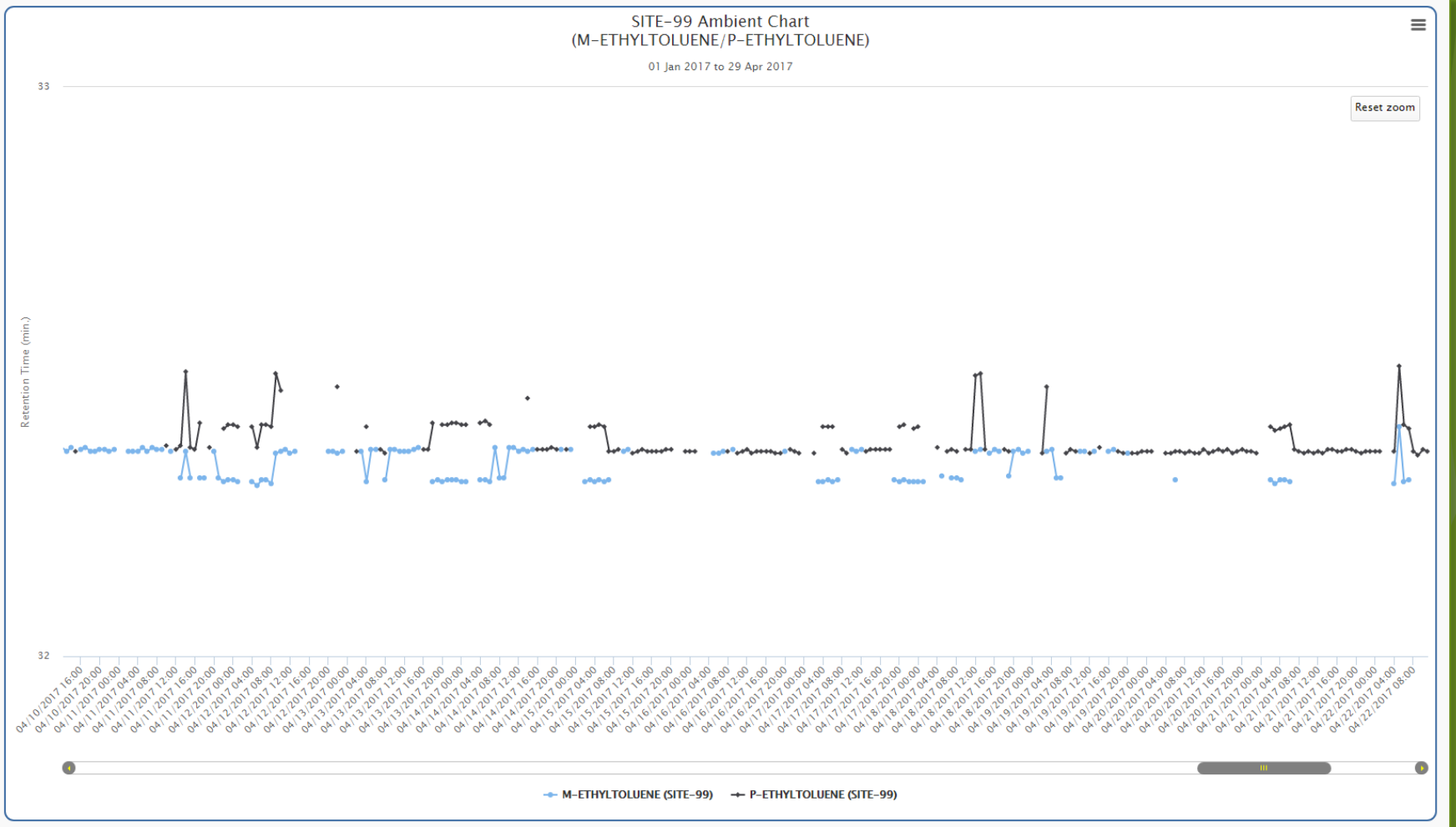
AutoGC Systems: Level II Data Review

Ambient Data – Time Series – Common Relationships

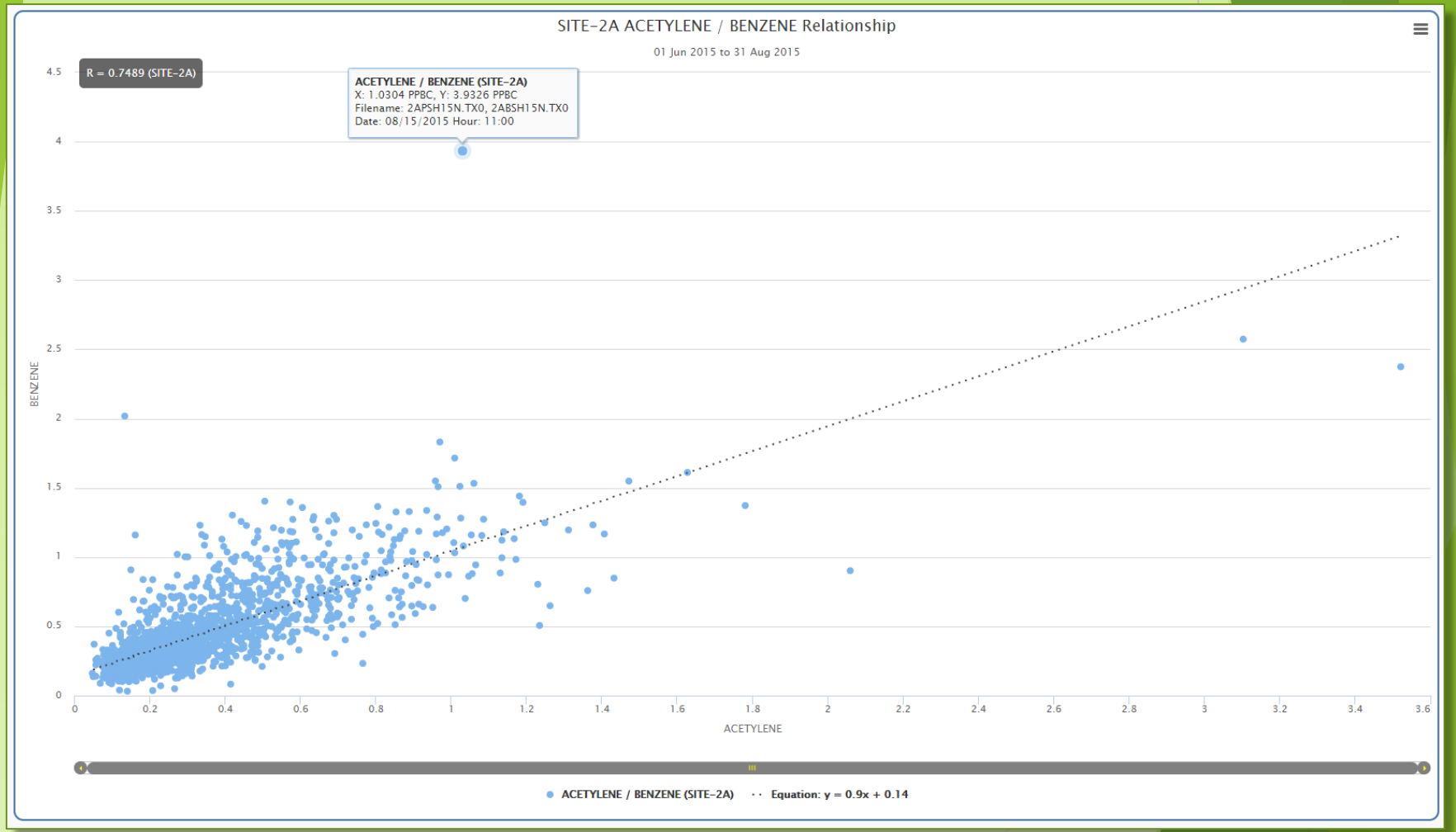


AutoGC Systems: Level II Data Review

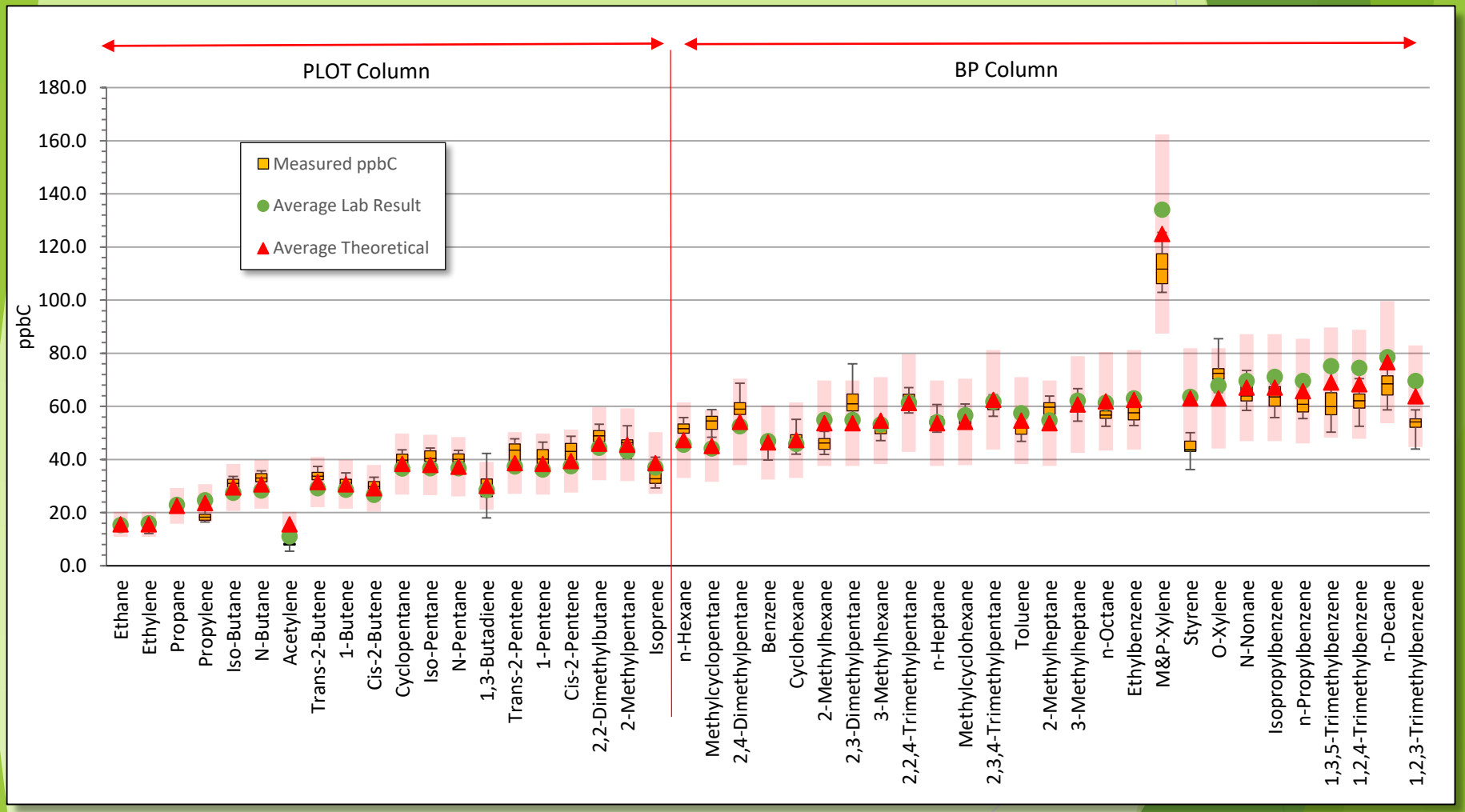
Ambient Data – Time Series – Retention Time Plots



AutoGC Systems: Level II Data Review
Ambient Data – Scatter Plots



AutoGC Systems: Level III Data Review Performance Evaluation Audits



Requirements for Successful AutoGC

- Chromatographic Data System
  - Capable of identification and quantitation of complex samples
  - Robust and simple calibration strategy
  - Output format for easy review of data
  - Event control for automation of quality control checks
- Standard Operating Procedures
  - Daily operations for consistent data collection
  - Validation to handle deviations consistently
- Data Quality Objectives
  - Well defined control limits
  - System for identifying and correcting failures

FIFTY SIX
NON-METHANE
HYDROCARBONS
TWENTY FOUR
HOURS A DAY
SEVEN
DAYS A WEEK

Acknowledgements

"Without data you are just another person with an opinion." ---W. Edwards Deming

Nicola Watson, Markes International

Kelly Beard, Agilent Technologies

✦✦✦

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Corey Whipp, PerkinElmer

✦✦✦

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